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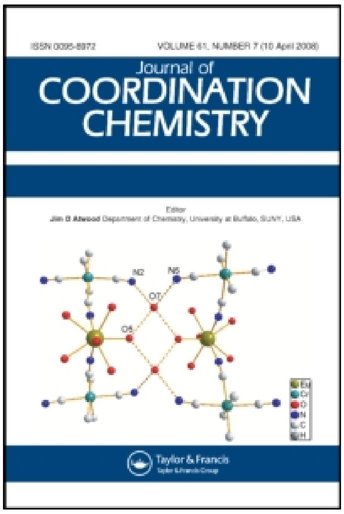

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A 3-D pillar-layered coordination polymer $\{[EuCu(C_2O_4)(na)_2] \cdot 2H_2O\}$<i><sub><i>n</i>: synthesis, structure and photoluminescent properties

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A 3-D pillar-layered coordination polymer $\{[EuCu(C_2O_4)(na)_2]\cdot 2H_2O\}_n$: synthesis, structure and photoluminescent properties

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A 3d–4f heterometallic coordination polymer, $\{[EuCu(C_2O_4)(na)_2]\cdot 2H_2O\}_n$ (**1**) [Hna=nicotinic acid], has been synthesized by hydrothermal reaction of lanthanide oxides, Cu(I), and pyridine-2,3-dicarboxylic acid. **1** features a 3-D pillar-layered coordination framework constructed from two-dimensional lanthanide-carboxylate layers and Cu(na) pillars. Interestingly, the na ligand was obtained by the *in situ* decarboxylation of pyridine-2,3-dicarboxylic acid.

Keywords: Synthesis; Structure; Coordination polymer; Photoluminescent properties

1. Introduction

Interest in designing and synthesizing mixed d-f complexes has intensified by their fascinating structural diversity and their potential applications in catalysis [1], magnetism [2], photochemical sensors [3] and adsorption [4]. Existing Ln–M coordination polymers were summarized and a classification proposed according to the different types of interactions between Ln–M: (a) Ln–M direct bonds, (b) ionic associations, and (c) Ln-linkers-M [5]. For the Ln-linkers-M system in particular, a typical strategy used to construct lanthanide-transition metal heterometallic complexes is self-assembly from mixed metal ions and organic ligands containing hybrid donor atoms such as cyanide [6], carbonyl [7], pyridine-carboxylate ligand [8] and amino acids [9]. To target Ln–M coordination polymers by design, metal ions can be preselected so as to impart various functional properties or predictable coordination geometries [10]; choice of ligands is also important. Among the various ligands, multidentate N– or O–donor ligands, such as pyridine (di)carboxylic acids, have drawn

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attention in the construction of Ln–M frameworks. For example, pyridine dicarboxylic ligands, including pyridine-2,6-, 2,5- or 3,4-dicarboxylic acids, have been employed in the construction of Ln–M frameworks [11]. Compared with other pyridine-dicarboxylic acids, pyridine-2,3-dicarboxylic acid is rarely used in construction of Ln–M frameworks [10, 12] and was chosen as the linker to construct Ln–M frameworks. *In situ* decarboxylation of pyridine-2,3-dicarboxylic acid occurs and pyridine-2,3-dicarboxylic acid is transformed into nicotinic acid. In this article, we report the synthesis, characterization, crystal structure, and photoluminescence of $\{[\mathrm{EuCu(C_2O_4)(na)_2}]\cdot 2\mathrm{H_2O}\}_n$ (1).

2. Experimental

2.1. *Materials and methods*

All reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. FT-IR spectra were recorded from KBr pellets in the 4000–400 $\mathrm{cm^{-1}}$ range on a Nicolet 5DX spectrometer. Emission spectra were recorded on a Perkin-Elmer LS50B fluorescence spectrophotometer.

2.2. *Hydrothermal synthesis*

Synthesis of complex $\{[\mathrm{EuCu(C_2O_4)(na)_2}]\cdot 2\mathrm{H_2O}\}_n$ (**1**) [Hna=nicotinic acid] is as follows: A mixture of $\mathrm{Eu_2O_3}$ (0.25 mmol, 88 mg), CuCl (0.2 mmol, 20 mg), oxalic acid (0.5 mmol, 63 mg), $\mathrm{H_2pydc}$ (1 mmol, 167 mg) and $\mathrm{H_2O}$ (14 mL) was placed in a 23 mL Teflon reactor, stirred for 30 min in air at room temperature and then kept under autogenous pressure at 453 K for 5 d. The mixture was cooled to room temperature at 5 $\mathrm{K\,h^{-1}}$. Colorless crystals of **1** were isolated by filtration, washed with distilled water, and dried in air (yield ca. 35%). Anal. Calcd. for $\mathrm{C_{14}H_{12}CuEuN_2O_{10}}$: C, 28.80; H, 2.07; N, 4.80. Found: C, 28.69; H, 2.12; N, 4.73. IR (KBr, $\mathrm{cm^{-1}}$): 3447(m), 1632(m), 1544(s), 1410(s), 1307(w), 1218(w), 1057(w), 855(w), 769(m), 687(m), 547(w).

2.3. *X-ray crystallography*

Single-crystal X-ray diffraction measurements were carried out on a Bruker P4 diffractometer at room temperature. Data collection was performed with Mo-Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least squares refinements, and the structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL [13]. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. Crystallographic data and experimental details for the structural analysis are summarized in table 1. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{14}H_{12}CuEuN_2O_{10}$
Formula weight	583.76
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	9.226(2)
b	21.606(3)
c	9.5587(14)
β	116.142(14)
V(Å^3)	1710.4(5)
Z	4
D_c (g cm^{-3})	2.267
μ (mm^{-1})	1.964
F(000)	1128
Crystal size (mm^3)	0.17 × 0.12 × 0.09
θ Range for data collection (°)	1.89 – 24.99
Reflections collected	3779
Independent reflections (R_{int})	3001(0.0295)
Max., min. transmission	0.6761, 0.4891
T (K)	293(2)
Goodness-of-fit on F^2	1.124
Data/restraints/parameters	3001/0/253
Final R indices $[I>2\sigma(I)]^a$	$R_1=0.0364$ $wR_2=0.0947$
R indices (all data)	$R_1=0.0455$ $wR_2=0.1082$
Largest diff. peak and hole (e Å^{-3})	1.152, −2.801

[a] $R_1=\sum\|F_o|-|F_c\|/\sum|F_o|$; $wR_2=\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

1			
Eu(1)–O(1)#1	2.317(5)	Eu (1)–O(8)#2	2.343(4)
Eu (1)– O(4)#3	2.351(4)	Eu (1)–O(7)	2.387(4)
Eu (1)– O(2)#4	2.410(5)	Eu (1)–O(3)#5	2.485(5)
Eu(1)–O(5)#6	2.525(4)	Eu(1)–O(6)	2.539(4)
Eu(1)–O(1)#4	3.129(5)	Cu(1)–O(5)	2.287(4)
Cu(1)–N(1)	1.888(5)	Cu(1)–N(2)	1.877(6)
Cu1–O6	2.756(4)	O(7)–Eu(1)–O(3)#5	76.11(16)
O(1)#1–Eu(1)–O(8)#2	86.75(17)	O(7)–Eu(1)–O(6)	119.77(15)
O(4)#3–Eu(1)–O(7)	133.42(16)	O(1)#1–Eu(1)–O(5)#6	137.96(15)
O(1)#1–Eu(1)–O(7)	142.81(16)	O(8)#2–Eu(1)–O(4)#3	144.64(16)
O(3)#5–Eu(1)–O(5)#6	150.19(15)	N(2)–Cu(1)–N(1)	153.3(2)
N(2)–Cu(1)–O(5)	101.8(2)	N(1)–Cu(1)–O(5)	104.5(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x,-y+5/2$, $z+1/2$; #2 $-x+2$, $-y+2$, $-z+2$; #3 $-x$, $-y+2$, $-z+1$; #4 $-x+1$, $y-1/2$, $-z+3/2$; #5 $x+1,y,z+1$; #6 $-x+1$, $-y+2$, $-z+1$.

3. Results and discussion

3.1. *Crystal structure*

X-ray structural analysis shows that **1** crystallizes in the monoclinic space group $P2_1/c$. As shown in figure 1, one Eu(III) center, one Cu(I) center, two half oxalate ligands and

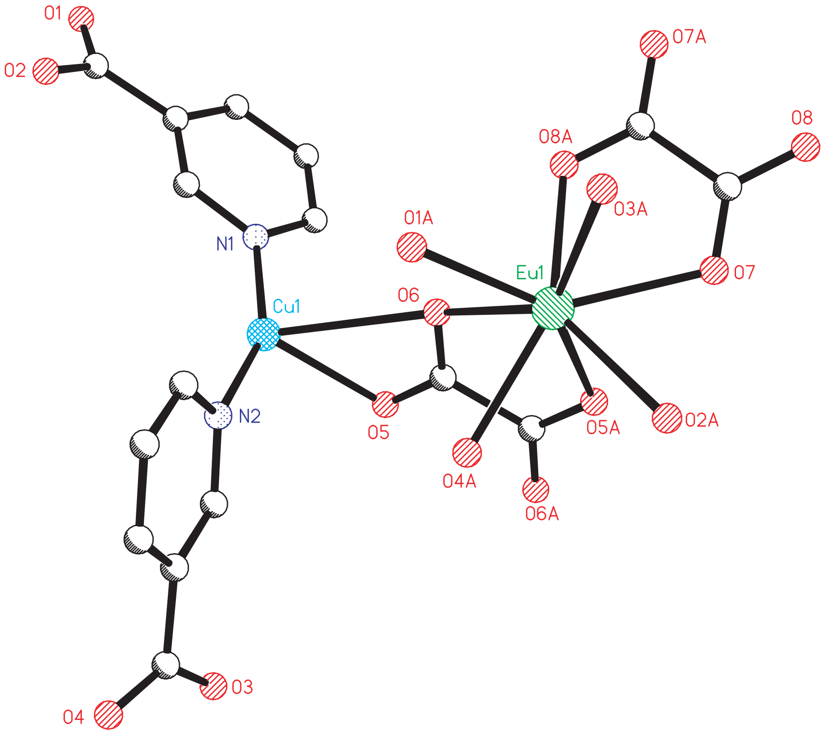
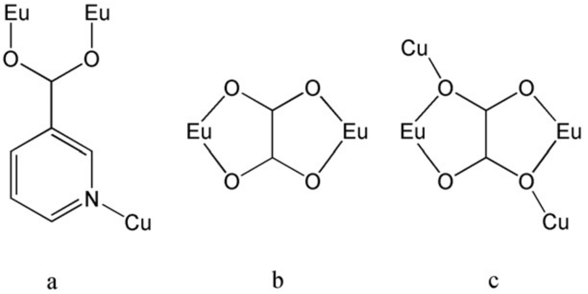


Figure 1. Coordination environment of the Cu(I) and Eu(III) ions in **1**.



Scheme 1. The coordination modes of na ligand and oxalate ligand in **1**.

two na ligands are in the asymmetrical unit. Each Eu(III) center in **1** is eight-coordinate with four oxygens from two oxalates and four oxygens from two na ligands. The coordination geometry around the Eu(III) center is dodecahedral with Eu–O bond lengths ranging from 2.317(5) to 2.539(4) Å and the O–Eu–O bond angles ranging from 44.27(14) to 150.19(15)°. The Cu(I) exhibits tetrahedral geometry coordinated by two nitrogens from two bridging na ligands [Cu1–N1 1.890(5) and Cu1–N2 1.878(6) Å] and two oxygens from oxalate [Cu1–O5 2.287(4), Cu1–O6 2.756(4) Å]. Two crystallographically unique na ligands exhibit the same coordination (scheme 1) as a tridentate bridging ligand coordinating one Cu(I) and two Eu(III) ions (scheme 1a). The oxalates have two coordination modes, one as *bis*(bidentate) linking two Eu(III)

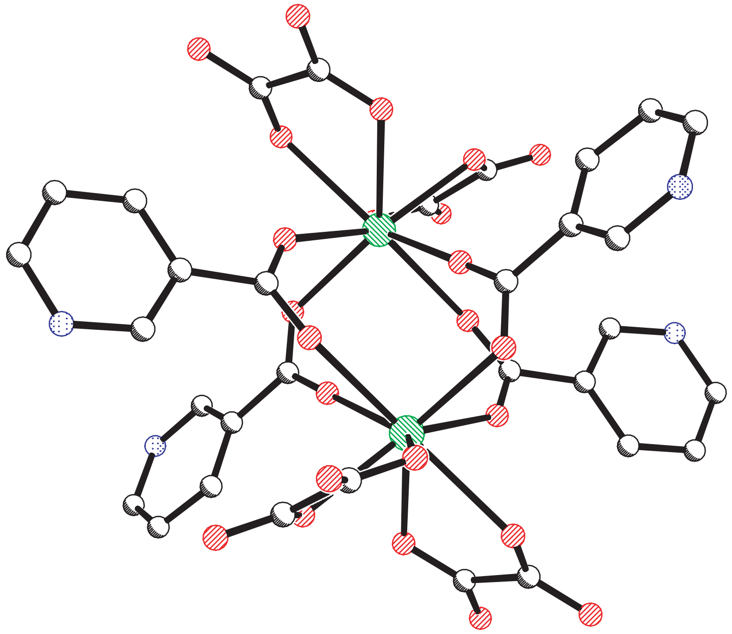


Figure 2. View of the binuclear $[Eu_2(C_2O_4)_4(na)_4]^{2-}$ subunit in **1**. All H atoms are omitted for clarity.

ions (scheme 1b) and the other tetradentate chelating and bridging two Eu(III) ions and two Cu(I) ions (scheme 1c). Two Eu(III) ions are linked by four carboxylate groups from four different na ligands *via syn-anti* bidentate bridging to form a binuclear $[Eu_2(C_2O_4)_4(na)_4]^{2-}$ subunit (figure 2), then the neighboring binuclear subunits are connected by oxalates to form a regular 2-D network parallel to the *ac* plane with hexa-membered ring arrays. The Eu$\cdots$Eu distance is 4.230(3) Å (within the binuclear subunit) and 5.981(3) Å (adjacent binuclear subunits). The 3-D pillar-layered frameworks are constructed by 2-D Eu-oxalate layers *via* [Cu(na)] pillars (figure 3).

3.2. *IR spectrum and TGA*

The IR spectra of **1** show characteristic bands of carboxylic groups at 1632 and 1544 cm^{-1} for the asymmetric stretching and at 1410 cm^{-1} for symmetric stretching. The separations (Δ) between $v_{asym}(CO_2)$ and $v_{sym}(CO_2)$ indicate that the carboxylic groups coordinate in a bridging fashion [14]. The absence of strong characteristic peaks around 1720 cm^{-1} indicates that all carboxylic groups are deprotonated [15, 16], consistent with the results of the X-ray analysis. Thermogravimetric analyses (TGA) indicates that **1** loses coordinated and lattice water molecules below 295°C (figure 4) with 6.25% weight loss, consistent with that calculated (6.17%).

3.3. *Photoluminescent properties*

Because of the excellent luminescent properties of Eu(III), the photoluminescent spectra of powder samples of **1** were measured at room temperature. When excited at 397 nm,

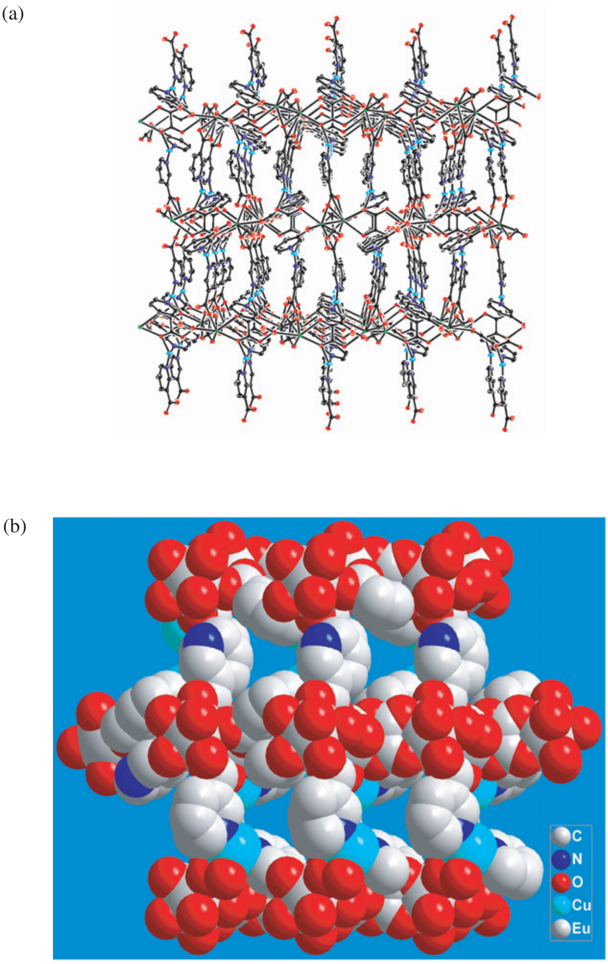


Figure 3. (a) The 3-D pillar-layered structure viewed along the *a*-axis of **1**. All H atoms are omitted for clarity. (b) Space-filling plots of the structure of **1** viewed along the *c*-axis.

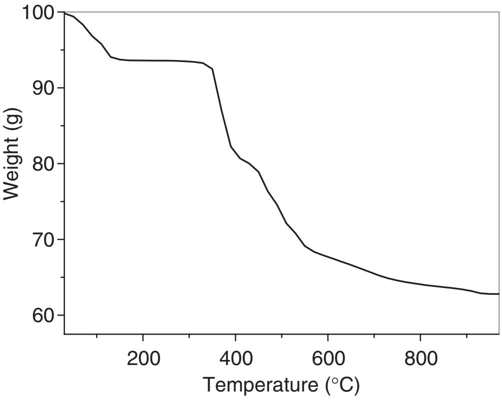


Figure 4. TGA curve of **1**.

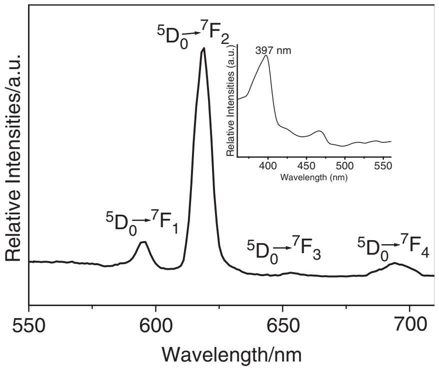


Figure 5. Solid-state emission spectrum for **1** at room temperature (excited at 397 nm).

1 emits red light (figure 5). The emission peaks of **1** at 595, 618, 651 and 695 nm can be assigned to $^5D_0 \rightarrow {}^7F_n$ ($n = 1$–4) transitions. For **1**, the $^5D_0 \rightarrow {}^7F_2$ transition at 618 nm is the preferred transition for Eu^{3+}-containing luminescent materials. The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition is widely used as a measure of the coordination state and the site symmetry of the europium ion, since the $^5D_0 \rightarrow {}^7F_1$ emission is relatively strong, independent of the ligand environment, and primarily magnetic dipole in character, while the the $^5D_0 \rightarrow {}^7F_2$ emission is essentially purely electric dipole in character, and its intensity is extremely sensitive to the crystal field symmetry [17]. In **1**, the $^5D_0 \rightarrow {}^7F_2$ transition is the strongest of the four transitions, with intensity ratio of 5.96 for $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$, showing that Eu(III) has a lower symmetry coordination environment in **1** [18], consistent with the single-crystal X-ray analysis.

Supplementary material

CCDC reference number is 662455. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int code +44(1223)336-033; Email: deposit@ccdc.cam.ac.uk].

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